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For various problems in physiology, especially that of the measurement of the blood flow through the lungs of man, as described by Krogh and Lindhard, it is necessary to analyze with great accuracy gas mixtures containing nitrous oxide. Krogh and Lindhard¹ in their paper on the blood flow describe a method of combustion of nitrous oxide with hydrogen, using a modified Haldane gas analysis apparatus.² Further details are given in subsequent papers by Krogh³ and by Lindhard.⁴ Their method is much simpler and more rapid than that described by Markoff, Müller, and Zuntz.⁵

Various text-books on gas analysis refer to the combustion method of nitrous oxide but do not give details by which it may be carried out, and in fact usually give the impression that the method is not one of great accuracy.

¹ Krogh and Lindhard: Measurement of the blood flow through the lungs of man. Skand. Archiv. f. Physiol., 1912, xxvii, p. 100.

² Haldane: Methods of air analysis. 1912, Griffin and Co., London.

³ Krogh: Funktionsuntersuchungen an den Lungen des Menschen mittelst gasanalytischer Methoden; Abderhalden: Handbuch der Biochem. Arbeitsmethoden, 1915, Urban and Schwarzenberg, pp. 550.

⁴ Lindhard: Concerning the influence of ultraviolet light on the circulation in man. Skand. Archiv. f. Physiol., 1913, xxx, 73-96; Lindhard: Effect of posture on the output of the heart. Skand. Archiv. f. Physiol., 1913, xxx, 395-408.

⁵ Markoff, Müller, and Zuntz: Eine Stickoxydul-Methode zur Bestimmung der umlaufenden Blutmenge in lebenden Körper. Ztschft. f. Balneologie, 1912, iv, 14-15.

In light of the article by Baskerville and Stevenson⁶ on the analysis of nitrous oxide in which, on the authority of Lunge,⁷ the combustion of nitrous oxide with hydrogen is stated to be unreliable, we determined to reinvestigate this point before proceeding to the use of the method in physiological work.

Deviation from the gas laws. Nitrous oxide is not a perfect gas and its deviation from the gas laws is considerable. At the usual temperatures and pressures existing in a laboratory it is of the order of 0.7 per cent. However, in the method of analysis by which nitrous oxide is combusted with hydrogen to form nitrogen and water and the contraction measured, the above deviation is automatically compensated as the following consideration shows. The litre weight of nitrous oxide at 0° and 760 mm., were it a perfect gas, would equal

$$\frac{\text{Molecular weight of nitrous oxide}}{\text{Molecular volume}} = \frac{44.014}{22.412} = 1.964 \text{ grams}$$

But the litre weight at 0° and 760 mm. is actually found to be 1.9777 grams.⁸ That is, at 0° and 760 mm. the deviation of nitrous oxide from the gas laws is $\frac{1.9777 - 1.964}{1.964} = 0.7$ per cent.

This error need not be taken into consideration in the analysis as shown by the following calculation. Let N be the number of molecules of hydrogen or nitrogen per cubic centimeter at the constant conditions of the experiment. Hydrogen is added in excess to 1 cc. of nitrous oxide. At 20° and 760 mm., 1 litre of nitrous oxide contains about 1.006 times as many molecules as nitrogen or hydrogen under the same conditions. In this case, 1.006 molecules of nitrous oxide must be decomposed, and therefore 1.006 molecules of hydrogen are required since



and as hydrogen is nearly "perfect" under these conditions, 1.006 cc. of hydrogen will be used up. But at the same time 1.006

⁶ Baskerville and Stevenson: Contributions to the chemistry of anaesthetics: nitrous oxide. Jour. Indust. and Eng. Chem., 1911, iii, 8.

⁷ Lunge: Ber. 14, 2188; Kemp: Chem. News, 71, 108 (1895).

⁸ Landolt and Bornstein: Physikalisch-Chemische Tabellen, 1912, p. 150.

molecules of nitrogen will be formed which will occupy 1.006 cc. So that we have

1.000 cc. N ₂ O disappeared	1.006 cc. N ₂ formed
1.006 cc. H ₂ disappeared	
2.006 cc. disappeared	1.006 cc. formed

Therefore the contraction equals 1.000 cc., just equal to the volume of nitrous oxide.

If the nitrous oxide were P per cent pure, the contraction would equal the volume of nitrous oxide present in the sample taken with great exactness.

The only errors lie in (1) the increase in "perfection" of nitrous oxide when mixed with an excess of hydrogen; (2) the "imperfection" of hydrogen; (3) the "imperfection" of nitrogen. These irregularities, however, are of the order of 0.05 per cent of the whole volume. And for the analysis of such small samples of nitrous oxide here described, which must be transferred, etc., this correction would be meaningless.⁹

Apparatus. For the analysis of nitrous oxide a carefully calibrated 10 cc. Haldane apparatus is used, modified as described by Krogh and Lindhard with a three-way hydrogen intake tap on the connecting piece leading to the combustion tube. The absorption pipette for carbon dioxide is filled with a concentrated solution of potash (sp. g. 1.55), instead of the usual 10 per cent solution. The alkaline pyrogallic solution must be very active, so that the oxygen will be quickly absorbed. The gas mixture should be carried into the potash and pyrogallic pipettes the same number of times in each analysis and check readings avoided. Under these conditions the error due to the solubility of nitrous oxide in these solutions is reduced to a point which is negligible when dealing with differences in percentages in dilute nitrous oxide mixtures.

The combustion tube is fitted with No. 35 platinum wire. For burning the nitrous oxide the wire should be bright red. A white heat is not necessary, but a dull red heat is not sufficient

⁹ We are indebted to Dr. G. Shannon Forbes, Assistant Professor of Chemistry, Harvard University, for this exposition of the behavior of nitrous oxide in relation to the gas laws and to the method of analysis.

to remove the last traces of nitrous oxide in an atmosphere consisting largely of hydrogen. In very dilute mixtures of nitrous oxide, when there is a large excess of hydrogen and only a comparatively small amount of nitrogen it is difficult to heat the wire to a bright red, as much more current is necessary under these conditions. For this reason we had to modify our resistance regulator so that a greater range of current strength was available.

Analysis of dilute mixtures. The analysis of mixtures containing a combined amount of oxygen and carbon dioxide not exceeding 22 per cent and 16 per cent of nitrous oxide can be made very readily and with great accuracy. Before proceeding with an analysis the apparatus should be tested for tightness by carrying through an air analysis, including the addition of hydrogen and heating of the combustion tube. This insures freeing the apparatus of carbon dioxide, oxygen, and nitrous oxide.

The sample is taken into the burette and measured. The carbon dioxide is absorbed by passing the sample back and forth into the potash tube eight times; the carbon dioxide contraction is then read. The oxygen is absorbed by passing the sample fifteen times into the pyrogallic, then washing the potash tube once, and again passing the sample into the pyrogallic eight times. The potash tube is once again washed and the sample is then finally passed into the pyrogallic eight times. The levels are adjusted and the oxygen contraction measured. About 2.5 cc. of hydrogen are drawn directly into the combustion tube and the platinum wire heated to remove all traces of oxygen. The hydrogen is then taken into the burette with the sample and the total volume measured. The mixture is combusted by passing the sample back and forth ten times over the heated platinum wire; the potash and pyrogallic tubes are washed once and the mixture passed into the combustion tube five times; the potash and pyrogallic tubes are again washed once each and the mixture combusted as before. The contraction is then read and this will be equivalent to the volume of nitrous oxide in the original sample. A check reading is made of this last volume, after again passing the gas into the potash and pyrogallic and combustion tubes.

Very constant results are obtained when the analyses are carried out according to a definite technic and care used in adjusting the various levels. The level of the mercury in the combustion tube should be made with the three-way tap in connection with the burette and potash tube, otherwise serious error may be introduced by the production of pressure differences when obtaining the mercury level. Furthermore the readings should not be made after a combustion until the combustion tube is cool. A complete analysis usually takes about twenty minutes.

The exactness of the method is shown by the following results obtained by analysis of two samples of the same mixture:

	<i>Sample I</i> per cent	<i>Sample II</i> per cent
CO ₂	0.10	0.10
O ₂	17.79	17.77
N ₂ O.....	15.21	15.19

Analysis of concentrated mixtures. For the analysis of concentrated mixtures of nitrous oxide the following modification is necessary. Before beginning an analysis the apparatus is filled with about 7.1 cc. of hydrogen and all traces of carbon dioxide, oxygen, and nitrous oxide removed by passing the gas back and forth into the various tubes and heating the platinum wire. The levels are carefully adjusted; the reading of the hydrogen volume (with more or less nitrogen) obtained; and then the hydrogen is carefully stored in the combustion tube. About 2.5 cc. of the nitrous oxide is drawn into the burette and the hydrogen is then brought back from the combustion tube into the burette. The levels are adjusted and the total volume read. The analysis is then carried through as described above.

If the nitrous oxide sample contains only very small amounts of carbon dioxide or oxygen, it is not fair to assume that the entire contraction observed on passing into the potash and pyrogallic pipettes is due to the presence of these gases because slight traces of nitrous oxide are absorbed by the solutions. For instance, in the following consecutive analyses of samples from the same tank of nitrous oxide, the first sample was analyzed as above; the second sample was passed through alkaline pyrogallic

before entering the burette and combusted directly without going into the potash or pyrogallic pipettes; the other six samples were combusted directly without ever being brought into contact with the potash or pyrogallic.

<i>Sample I</i>	<i>Sample II</i>	<i>Samples III to VIII</i>
Entering potash and pyrogallic tubes, then combusting	Bubbling first through pyrogallic and then com- busting directly	Combusting directly without coming into contact with either potash or pyrogallic
<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
CO ₂ 0.21		N ₂ O..... 98.8
		N ₂ O..... 99.1
		N ₂ O..... 97.6
O ₂ 0.57		N ₂ O..... 97.9
		N ₂ O..... 98.5
N ₂ O..... 97.28		N ₂ O..... 98.4
Total..... 98.1	N ₂ O..... 98.6	N ₂ O..... 98.3

As the total contraction of samples I and II fall within the variations shown by samples III to VIII it is evident that the nitrous oxide contains no appreciable trace of oxygen; for by the combustion method with hydrogen, if oxygen were present, its contraction volume would be three times its actual volume and the above agreement would be impossible if there were any appreciable amount of oxygen present in the samples. The method does not admit of the determination of less than 0.1 per cent of oxygen.

The presence of an appreciable amount of carbon dioxide is ruled out by passing the gas through baryta water.

Therefore we feel justified in concluding that the tank from which the above samples of nitrous oxide were obtained contained ~~98.3~~ per cent nitrous oxide and ~~1.7~~ per cent nitrogen (argon or other noncombustible gases) with no appreciable amount of carbon dioxide or oxygen.

The method is particularly serviceable for analyzing commercial nitrous oxide used for anaesthetic purposes when the proportions of nitrous oxide, oxygen, carbon dioxide, and nitrogen are desired; it is not suitable for detecting traces of these or other contaminating gases.

SUMMARY

The details are given of analysis of nitrous oxide by the method of combusting with hydrogen with the use of a modified Haldane apparatus.

The accidental errors of the method for dilute mixtures of nitrous oxide are slightly greater than are those for the analysis of air in a Haldane apparatus on account of the necessity of adding hydrogen and using the combustion tube. Furthermore there is a slight constant error caused by the absorption of nitrous oxide by the potash and pyrogallic solutions. As this error is practically the same in consecutive samples, if an identical analytical routine is used it can be neglected when comparative percentages are desired.

For the analysis of concentrated mixtures of nitrous oxide the Haldane apparatus does not admit of the use of a sample exceeding 2.5 cc. In consequence the errors of the apparatus as well as those of absorption are much magnified. As the errors of the apparatus are accidental the average of several analyses will minimize their importance. Duplicate analyses with and without the use of potash and pyrogallic, as well as analysis of samples collected over pyrogallic will allow the determination of the absorption error. A series of eight such analyses from the same commercial nitrous oxide tank gave an average of 98.4 per cent of nitrous oxide, the balance being nitrogen (argon or other non-combustible gases); the extremes were 97.6 per cent and 99.1 per cent. By taking the average of several analyses the purity of a sample of nitrous oxide can be determined by this method with an accuracy sufficient for most physiological purposes.

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